

# **CERTIFICATION OF APPROVAL**


## **Study of the Effect of Precipitation Inhibitor on Static and Dynamic Surfactant Adsorption Using High Salinity Injection Water**

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A project dissertation submitted to the:  
**Petroleum Engineering Programme**  
**Universiti Teknologi PETRONAS**

in partial fulfilment of the requirement for the:  
**Bachelor of Engineering (Hons)**  
**(Petroleum Engineering)**

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January 2011

## CERTIFICATION OF ORIGINALITY

This is to certify that I am responsible for the work submitted in this project, that the original work is my own except as specified in the references and acknowledgements, and that the original work contained herein have not been undertaken or done by unspecified sources or persons.



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MOHAMMAD AZWAN SHAHMEE

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## 1. Abstract

Adsorption of surfactants from aqueous solutions in porous media is very important in enhanced oil recovery (EOR) of oil reservoirs because surfactant loss due to adsorption on the reservoir rocks impairs the effectiveness of the chemical slurry injected to reduce the oil–water interfacial tension (IFT) and renders the process economically unfeasible. Surfactant adsorption is due to the different charges between slug and rock that will create attraction force. The different charges between the slug and rocks can be solved by increasing the pH of the slug. New developed method for surfactant formulation which is AAS is to overcome the problem of precipitation when using hard brine or high salinity water. In AAS, acid and alkali will react to form a salt that will coat the metal divalent ions such as magnesium and calcium from reacting with surfactant and alkali to form insoluble precipitation [1]. So, this research will study the effect of precipitation inhibitor (PI) on the surfactant adsorption using high salinity water injection. Surfactant that will be used is Alpha Olefin Sulfonate which is anionic surfactant. The acid and alkali are used are acrylic acid and sodium hydroxide. The surfactant adsorption will be measured in two different methods which are static and dynamic. For the static method, the experiment will be divided into 3 phases which are first phases is to find the optimum concentration of surfactant, second phase is to find the optimum concentration of the alkali and the third phase is to find the optimum concentration of acid. For dynamic method, the experiment will be conducted by varying the acid concentration in the surfactant solution that already included optimum concentration of surfactant and alkali. The surfactant concentration after each test will be measured by using two phase titration which will use Hyamine 1622 as titrant and mixed acid as indicator.

## 2. Introduction

Enhanced Oil Recovery (EOR) is methods attempt to improve the extraction of crude oil by injecting different kinds of materials that can change selected properties of physics and chemistry of fluid (water and oil) in the reservoir rocks [2].

According to Pinczewski (1993) and Ershagi (1994), the processes in the EOR can be classified into 3 major categories. Respectively – these methods have their own characteristics – themselves mainly related to the type of oil remaining to be taken and reservoir characteristics (rock where the oil is) [3].

<b>Chemical</b>	Surfactant flooding, Micellar Polymer Flooding, Polymer Flooding
<b>Thermal</b>	Steam Flooding, Fire Flooding
<b>Miscible</b>	Carbon Dioxides Flooding, Nitrogen and Flue Gas Flooding

One of the major problems in surfactant flooding is surfactant adsorption from solution onto solid surfaces most commonly occurs in porous media either on the walls of pores or throats or else on fine particle in rock pores. This adsorption constitutes a loss of valuable surfactant so it directly affects and may well dictate the economics of an oil recovery or remediation process. Surfactant adsorption is due to the different charges between rock and slug which will create attraction force [4].

ASP is one of surfactant flooding which stand for Alkali-Surfactant-Polymer. The combination involving alkali-surfactant-polymer (ASP) has been recognized as a cost effective chemical flooding process for light and medium oils [5]. In the ASP process, alkali is used to make an in-situ surfactant with acidic components of the crude oil and increases the pH to lower surfactant adsorption [15]. Surfactants are used to lower the IFT between oil and water while polymer is used to improve sweep efficiency by providing mobility control [6]. Using a combination of these chemicals, the oil recovery is greatly enhanced by decreasing IFT, increasing capillary number and improving mobility ratio [7].

Due to reaction between alkali and calcium and magnesium ions, fresh water must be used to produce compatible ASP. But, this will not prevent the reaction due to the appearance of the ions in the formation water in the reservoir. To overcome this problem, new formula AAS (Acid Alkali Surfactant) is formulated to overcome precipitation problem. Precipitation inhibitor will be produced from reaction between acid and alkali and will coat the calcium and magnesium ions that will prevent them from reacting with alkali and surfactant.

### 3. Problem Statement

The loss of surfactant from the main chemical slurry during surfactant flooding is a major determinant in process performance and economy. It has been shown that the nature of the adsorption isotherm depends to a large extent on the type of surfactant used, the morphological and mineralogical characteristics of the rock, the type of electrolytes present in solution and, also, of co surfactants and alcohols. The adsorption of surfactants can be affected by the charge on the rock surface and fluid interfaces [8, 9]. The slug that is injected which formulated by using ASP has negative charges. Meanwhile, the rock has positive charges. These different charges will create attraction force that will make surfactant to be adsorbed by the rock. The surfactant that be adsorbed will reduce the surfactant concentration thus will reduce the effectiveness of the surfactant to reduce the IFT. Based on conventional ASP method, alkali is been introduced to the reservoir before introducing the surfactant. By using alkali, it will increase the pH and change the pH of the solution and the charges around the rock. So, it will create a repulsion force and will make the surfactant not to be absorbed by the rock. So, the main component in reducing surfactant adsorption is pH of the slug.

But, to be able to use ASP method, the formulation needs fresh water which has low hardness level. This is due to the hard brine will create precipitation due to reaction between surfactant and metal divalent cations such as calcium and magnesium. The precipitation is insoluble and will create problem such as decreasing the effectiveness of surfactant to reduce IFT. So, new formulation is introduced which is AAS(Acid Alkali Surfactant) [1]. This new formulation will introduced acid to the slug that will react with the sodium ions (from alkali) and create sodium salt that will coat the metal divalent cations from reacting with the surfactant to form precipitation. However, since AAS uses acid as one of the component, it will reduce the pH of the slug. The pH of the slug is inversely acting with surfactant adsorption. As the pH increases, the surfactant adsorption will decrease.

#### **4. Objective and Scope of Study**

**Objectives:**

- I. To study the effect of precipitation inhibitor on surfactant adsorption using static method.
- II. To study the effect of precipitation inhibitor on surfactant adsorption using dynamic method.

**Scope of Study:**

- I. Surfactant adsorption
- II. Alkali – Surfactant Adsorption
- III. Precipitation Inhibitor – Surfactant Adsorption
- IV. Static and Dynamic Method



## **5. Literature Review**

### **Oil Production Recovery**

There are three kind of oil production recovery to get maximum product in oil exploration.

#### **Primary recovery**

Oil production only uses the existing power in the reservoir (natural water movement, gas expansion cork, the movement of dissolved gases, and changes in pressure)

#### **Secondary recovery**

Oil production by providing gas or water injection to push the oil out, the basic concept is to keep the pressure of the reservoir same as in primary recovery.

#### **Tertiary recovery**

Any process that can take oil from the reservoir with a better job than conventional technologies (primary and secondary recovery), and generally use the fluids more effective, and is called the recovery agent.

Factors leading to the availability of oil is broadly because the reservoir rock's heterogeneity. In the reservoir can be contacted by fluid pressure, not all oil can be washed away, in part, between 10% – 40% of pore volume remained stuck in the pores due to capillary pressure ( $P_c$ ) and the interface tension (IFT) is too large. And the last oil viscosity is too large, also can hinder the flow rate to be produced economically [10]

## **Surfactant Flooding**

Surfactant use for oil recovery is not recent development in petroleum field. De groot was granted a patent in 1929 claiming water-soluble surfactants as an aid to improve oil recovery [11]. The success of the surfactant factors such as formulation, cost of surfactants, availability of chemicals, environmental impact and oil prices in the market. In enhanced oil recovery, surfactant can be used in several formulations.

The selection of surfactants for enhanced oil recovery needs laboratory testing with crude oil and some chemical components like polymer, alkaline, and co-surfactant. Wangqi and Dave [12].

## **Alkaline Flooding**

Alkaline flooding and its variants are enhanced oil recovery processes that have for many years, been employed to recover residual oil. Oil recovery mechanisms are complicated. The mechanisms are such as emulsification with entrapment, entrainment, emulsification with coalescence, wettability reversal, wettability gradients, oil phase swelling disruption of rigid films and low interfacial tensions[13]. The alkali technique can be differentiated with other method that the chemicals promoting oil recovery are generated in situ by saponification. The acid number of oil is one of the most important things in alkaline flooding. Acid number is defined as the milligrams of potassium hydroxide to neutralize one gram of crude oil.

Wettability is also crucial in alkaline flooding which controls the initial distribution of residual oil in the pore space [14]. The main idea of wettability alteration is to reduce the capillary forces that hold the oil in the reservoir rock. In the original wetting state of medium , the non wetting phase occupies large pores and the wetting phase occupies the small pores Depending on the rock mineralogy alkali can interact with reservoir rock in several ways, which include surface exchange and hydrolysis and with the hardness ions in the fluid and those exchanged with rock surface.

### **Alkali-Surfactant-Polymer Flooding**

ASP flooding has been found as one of major EOR technique that can be successfully enough used in producing light and medium oils after conventional methods. The advantage of using ASP is ASP can be used for low acid number crudes while alkaline flooding can only be used with medium to high acid number. In the ASP process, alkali can be used to make an in-situ surfactant with acidic oils and increases the pH to lower surfactant adsorption. Surfactants are used to lower the IFT between oil and water while polymer is used to improve sweep efficiency by providing mobility control [10]. In the ASP process, alkali is used to make an in-situ surfactant with acidic components of the crude oil and increases the pH to lower surfactant adsorption [15].

### **Surfactant adsorption**

Surfactant adsorption is one of the major problems in chemical flooding which involve surfactant. Too much loss of surfactant on reservoir rocks would quickly diminish the life of surfactant in the displacement process. The most important cause of ionic surfactants adsorbing onto a solid is the electrical interaction between the charged solid surface and surfactant ions, which can be explained by electrical double layer theory [15]. The forces of adsorption due to electrostatic attraction or repulsion between a charged solid surface and the charged surfactant can play a governing role in the system with oppositely charged solid and surfactant. The occurrence of surface charge on the mineral particles is considered to be due either to preferential dissolution or hydrolysis of surface species followed by pH dependent dissociation of surface hydroxyl group [16].

The amount of adsorbed surfactant depends on the surfactant character, the rock properties, pH, potential determining ion in solution and salinity [16]. The pH may alter the surface charge to change the adsorption amount and the salinity may change the electrical potential of surface sites for the adsorption. It is well known that surfactant adsorption increases with the increases of surfactant concentration in solution until surfactant

concentration reaches a certain level. After that concentration level is reached, surfactant adsorption will no longer change with surfactant concentration. The surfactant, especially for a multi component surfactant mixture, often contains a second or even a third layer of molecular adsorption on a solid surface. This will increase the adsorption to a greater degree than that required for the formation of monolayer.

#### **Factor affecting surfactant adsorption**

- 1 Temperature
- 2 pH,
- 3 Salinity,
- 4 Type of surfactant
- 5 Types of solids found in the reservoir
- 6 Type of water

*by: Surfactants: fundamentals and applications in the petroleum industry*

#### **The effect of PI on surfactant Adsorption**

Surfactant adsorption is the phenomena when the surfactants are been absorbed by the rock. This is due to the different charges between the rock and surfactant that will create attraction force and the surfactant will be absorbed by the rock. Alkali will be introduced to increase pH of the surfactant. This will change the charges of the rock to the negative charges and will create repulsion force between rock and surfactant [17]. Alkali will be introduced to the surfactant to increase pH of the surfactant. This will change the charges of the rock to the negative charges and will create repulsion force between rock and surfactant). In the ASP process, it is theorized that the alkali reacts with the small amounts of acids and esters present in the crude oil to form surfactant in-situ. The alkali is also claimed to reduce the amount of surfactant adsorption onto the formation especially in limestone reservoirs. By increasing the

pH the iso-electric point of the formation is exceeded the surface becomes negatively charged. This increases the electrostatic repulsion between the rock surface and the negatively charged anionic surfactants and thus reduces adsorption [18]. But, the new proposed way is to use high salinity water to create the slug. But, high salinity water contains metal divalent cation that will react with the alkali and form precipitation. So, the aim to lower the solution pH cannot be achieved. So, the aim to lower the solution pH cannot be achieved. Therefore, acid is been introduced to react with the alkali and form a salt for that acid. This salt is known as precipitation inhibitor that will prevent surfactant and alkali from reacting with the divalent cations such as Ca and Ma. PI will create a thin layer around the metal divalent cations which will prevent them for reacting with the surfactant and alkali [18]

## 6. Apparatus

### Material Description:

The alkali used is sodium carbonate which is strong alkali. The acid used is acrylic acid. It is a weak polymer acid and widely use as a precipitation inhibitor. Alpha Olefin Sulfonate is used as anionic surfactant which has molecular weight around 340 mol/g. Synthetic brine that is used is 35000 ppm .

For two phase titration method, Hyamine 1622 is used as titrant which its molarity is 0.004 M. Mixed Acid Indicator is used as indicator. Chloroform is used as organic solvent.

Core description is as below;

	Core 1	Core 2	Core 3
Diameter (mm)	38.05	37.91	38.11
Length (mm)	77.23	71.21	74.59
Weight (g)	210.718	174.297	183.392
Permeability (md)	169.421	65.361	65.68
Grain density (g/cc)	2.96	2.621	2.592
V bulk (cc)	87.818	80.378	85.084
V grain (cc)	71.183	66.494	70.745
Porosity (%)	18.942	15.39	16.853
Pore volume (cc)	16.635	13.884	14.339

## 7. Methodology

### 6.1. Material Preparations

#### Brine

1. To prepare 5000ppm of brine, pour 1000 ml of distilled water in a beaker.
2. Place 10.422 grams of sodium chloride, 4.184 grams of magnesium chloride hydrate and 1.467 grams calcium chloride hydrate inside the beaker filled with 1000ml of distilled water. (refer to appendix B example of salt mass calculation)
3. Stirred the beaker slowly and gradually heat up the mixture to accelerate salts dissolves in the distilled water. Ensure during heating, the temperature does not exceed or reach boiling temperature to avoid evaporation.
4. After all salts have been dissolves, allow the brine to cool down.

### 6.2 Static Method

The experiments are divided into three phases with different aims

- I. 1<sup>st</sup> phase: To find optimum concentration of surfactant
- II. 2<sup>nd</sup> phase: To find optimum concentration of alkali
- III. 3<sup>rd</sup> phase: To find optimum concentration of acid

### 1<sup>st</sup> phase: To find optimum concentration of surfactant

1. Surfactant solutions are prepared with different concentrations which are 0.2, 0.4, 0.6, 0.8 and 1 % with each concentration in 20 ml of brine in 100 ml bottles which have plastic cap. The component is only surfactant. (refer to Appendix A)
2. Then, each solution will be measured pH by using pH meter and record the pH.
3. Measure the density for each solution by using density meter.
4. Calculate the mass of the sand needed. The ratio of liquid and solid must be equal to 1. Mass of sand can be calculated;  
$$mass_{sand} = Density_{solution} * Volume_{solution}$$
5. Then, the sand is put in the bottles which contained the slug and stirred by using magnetic stirrer. This will allow the slug and surfactant to achieve full contact between them
6. The bottle is close with cap and makes sure no leaking in the bottle. This is due to avoid surfactant lost due to evaporation in the oven.
7. Make a mark and glued it outside the bottle to make sure the volume surfactant before is same with the volume of surfactant after 3 days.
8. The bottles is put in the oven and set the temperature to 80 Celcius. Leave the bottle for 3 days.
9. After 3 days, check the volume of surfactant was decreasing or not. If there was decreasing in the volume, we need to repeat the experiment.
10. Take 10 ml of surfactant and put into new bottle and continue with two phase titration. ( see 5.4)
11. After that, the result is recorded and finds the optimum concentration of surfactant from the plot.

### 2<sup>nd</sup> phase: To find optimum concentration of alkali

1. Continue with second phase after get the optimum concentration of surfactant which is 0.6 %. Surfactant solutions are prepared with 0.6% of surfactant and different concentrations of alkali which are 0, 0.2, 0.4, 0.6, 0.8 and 1 % with each concentration in 20 ml of brine in 100 ml bottles which have plastic cap. The components are surfactant and alkali. (refer to Appendix A)
2. Then, each solution will be measured pH by using pH meter and record the pH.
3. Measure the density for each solution by using density meter.
4. Calculate the mass of the sand needed. The ratio of liquid and solid must be equal to 1. Mass of sand can be calculated;

$$mass_{sand} = Density_{solution} * Volume_{solution}$$

5. Then, the sand is put in the bottles which contained the slug and stirred by using magnetic stirrer. This will allow the slug and surfactant to achieve full contact between them
6. The bottle is close with cap and makes sure no leaking in the bottle. This is due to avoid surfactant lost due to evaporation in the oven.
7. Make a mark and glued it outside the bottle to make sure the volume surfactant before is same with the volume of surfactant after 3 days.
8. The bottles is put in the oven and set the temperature to 80 Celcius. Leave the bottle for 3 days.
9. After 3 days, check the volume of surfactant was decreasing or not. If there was decreasing in the volume, we need to repeat the experiment.
10. Take 10 ml of surfactant and put into new bottle and continue with two phase titration. ( see 5.4)
11. After that, the result is recorded and finds the optimum concentration of alkali from the plot.

### **3<sup>rd</sup> phase: To find optimum concentration of acid**

1. Continue with second phase after get the optimum concentration of surfactant which is 0.6 %. Surfactant solutions are prepared with 0.6% of surfactant, 0.6% of alkali and different concentrations of acid which are 0, 0.2, 0.4, 0.6, 0.8 and 1 % with each concentration in 20 ml of brine in 100 ml bottles which have plastic cap. The components are surfactant, acid and alkali. (refer to Appendix A)
2. Then, each solution will be measured pH by using pH meter and record the pH.
3. Measure the density for each solution by using density meter.
4. Calculate the mass of the sand needed. The ratio of liquid and solid must be equal to 1. Mass of sand can be calculated;
 
$$mass_{sand} = Density_{solution} * Volume_{solution}$$
5. Then, the sand is put in the bottles which contained the slug and stirred by using magnetic stirrer. This will allow the slug and surfactant to achieve full contact between them
6. The bottle is close with cap and makes sure no leaking in the bottle. This is due to avoid surfactant lost due to evaporation in the oven.
7. Make a mark and glued it outside the bottle to make sure the volume surfactant before is same with the volume of surfactant after 3 days.
8. The bottles is put in the oven and set the temperature to 80 Celcius. Leave the bottle for 3 days.



9. After 3 days, check the volume of surfactant was decreasing or not. If there was decreasing in the volume, we need to repeat the experiment.
10. Take 10 ml of surfactant and put into new bottle and continue with two phase titration. ( see 5.4)
11. After that, the result is recorded and finds the optimum concentration of alkali from the plot.



*Example of sample preparation for static method*

### 6.3 Dynamic Method

1. Clean the core with toluene solution for 1 days and dry it in the oven
2. Measure the core permeability and porosity by using Poroperm (refer to Appendix D)
3. Saturate the core with the brine for 1 day.
4. Surfactant solutions are prepared with 0.6% of surfactant, 0.6% of alkali and different concentrations of acid which are 0, 0.2, 0.4, 0.6, 0.8 and 1 % with each concentration in 100 ml of brine in 100 ml bottles which have plastic cap. The components are surfactant, acid and alkali
5. Then, each solution will be measured pH by using pH meter and record the pH.
6. Measure the density for each solution by using density meter.
7. Prepare core flooding equipment. The equipment is used is Benchtop Permeability System (BPS).(See Appendix D)
8. Inject the surfactant solution at 0.5 ml/min flow rate. Flow rate needs to be slow to allow the surfactant adsorption happened.
9. Check the pore volume from the Poroperm test. Collect the first produced fluid which equal to the pore volume.

10. Then, the produced fluid after it can be used for two phase titration to measure the left surfactant concentration.

#### 6.4 Surfactant Concentration Measurement Method

##### Two phase titration method

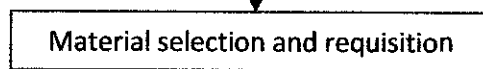
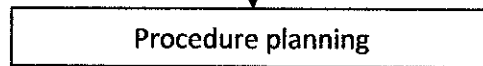
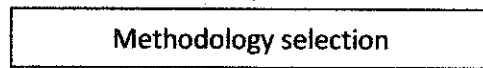
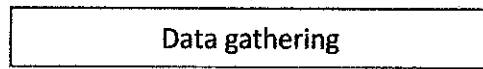
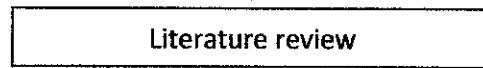
1. Fix the burette into the burette holder, and then fill the burette with Hyamine 1622 0.004 M solution. Record the volume in the burette
2. Then, prepare the organic solvent which is chloroform and mixed acid indicator. Measure 10 ml of chloroform and 10ml of mixed acid indicator and mix them in a small beaker
3. Take the bottle which contains 4 ml surfactant solution and mix with the solution in the small beaker. The solution forms two layer which aqueous phase at top and organic phase at bottom. The initial colour is faint pink in bottom layer.
4. Then, put the bottle under the burette and slowly added Hyamine 1662 solution by increment of 0.1 ml.
5. Make sure for each increment, shake the bottle to make sure the solution mix and reaches equilibrium.
6. Investigate the color changes of solution between aqueous phase and organic phase. The final color will be faint blue in bottom layer and titration is done.
7. Record the volume of Hyamine solution in the burette after the titration is done. Refer to Appendix C for Surfactant Concentration Calculation

*Based on Paper D 3049- 89, Standard Test Method for Synthetic Anionic Ingredient By Cationic Surfactant.*

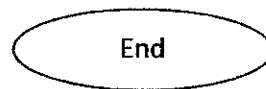
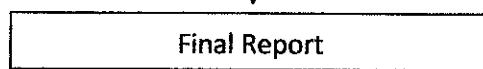
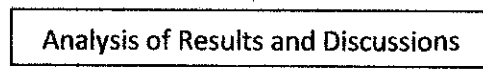
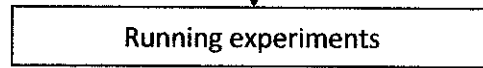
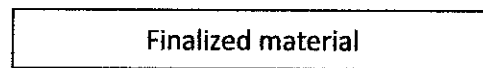
#### **Key Milestone**

In completing the project, student plays an important role as an investigator/researcher; doing all the literature study and look for his/her own approach to work on the topic. Thus, assistance and supervision from the assigned supervisor is essential to ensure the student is on the right path and follow the schedule. This could be done through a good communication medium such as weekly meeting, progress report and consultations. Progress report shall be submitted according to the schedule so that any corrective measure can be taken and indirectly both student and supervisor will have good and up-to-date information.

Final Year Project I



Final Year Project II



## Procedure Identification

### Gantt Chart For FYP II

No.	Activities /Week	1	2	3	4	5	6	7	8	9	10	11
1	Finalizing Material	■	■									
2	Finalizing Procedure	■	■									
3	Static Method		■	■	■							
4	Dynamic Method					■	■	■				
5	Progress Report Submission								■	■		
6	Continue undone project									■	■	■
9	All Results Gathering									■	■	■
	Draft Final Report									■	■	■
10	Submission									■	■	■
11	Submission of Final Report										■	■
12	Oral Presentation										■	■

## 8. Result and Discussion

### Surfactant Condition

Components	Surfactant Condition after 1 hour
0.2 Surfactant	Precipitation
0.4 Surfactant	Precipitation
0.6 Surfactant	Precipitation
0.8 Surfactant	Precipitation
1.0 Surfactant	Precipitation
0.6 Surfactant + 0.2 Alkali	Precipitation
0.6 Surfactant + 0.4 Alkali	Precipitation
0.6 Surfactant + 0.6 Alkali	Precipitation
0.6 Surfactant + 0.8 Alkali	Precipitation
0.6 Surfactant + 1.0 Alkali	Precipitation
0.6 Surfactant + 0.6 Alkali + 0.2 Acid	Cloudy
0.6 Surfactant + 0.6 Alkali + 0.4 Acid	Cloudy
0.6 Surfactant + 0.6 Alkali + 0.6 Acid	No precipitation
0.6 Surfactant + 0.6 Alkali + 0.8 Acid	No precipitation
0.6 Surfactant + 0.6 Alkali + 1.0 Acid	No precipitation

## Static Method Result:

To find optimum concentration of surfactant

Table 1: To find optimum concentration of surfactant

Surfactant concentration (%)	0.2	0.4	0.6	0.8	1
Weight of surfactant(g)	0.04	0.08	0.12	0.16	0.2
Volume of Brine(ml)	20	20	20	20	20
Density(g/cc)	1.0671	1.0675	1.0683	1.0692	1.0701
pH	6.44	7.1	7.44	7.66	7.78
Weight of sand(g)	21.342	21.356	21.366	21.384	21.402
Molarity of surfactant solution(M)	0.0056	0.0112	0.0168	0.0224	0.028
Volume of surfatant solution(3 days) taking for test	4	4	4	4	4
Used Hyamine (ml)	2.8	5.4	10	14	19
Molarity of surfactant solution(M)	0.0028	0.0054	0.01	0.014	0.019
Convert to %	0.1	0.22333	0.357	0.4998	0.6783
Surfactant Remaining (mg)	19.992	21.356	71.4	99.96	135.66
Surfactant Lost (mg)	20.008	24.304	48.6	60.04	64.34
Surfactant Lost /Weight of Sand (mg/g)	0.9375	1.6029	2.2746	2.8077	3.0063

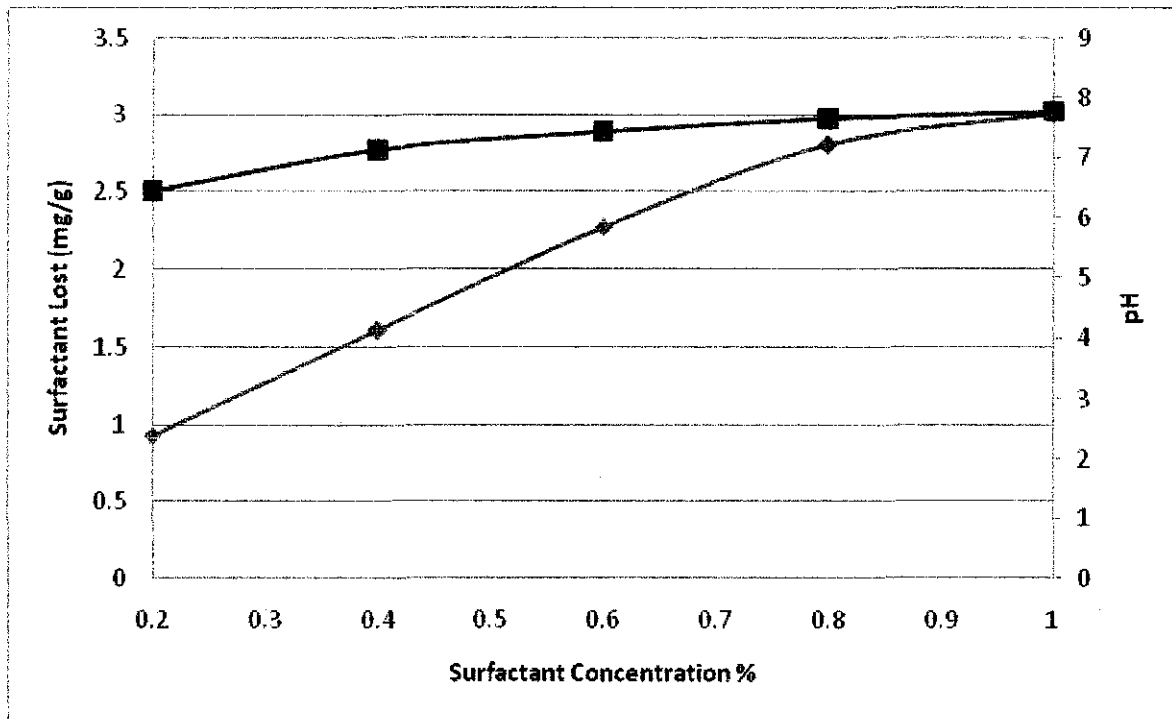


Figure 1: To find optimum concentration of surfactant

Figure 1 shows the effect of surfactant concentration on surfactant adsorption with the use of brine water. From the plot, the blue line is for surfactant lost versus alkali concentration and the red line is for pH versus alkali concentration. We can see the surfactant adsorption increases as the surfactant concentration increases until it reaches 0.8% which the increment rate becomes low. This is due to at certain surfactant concentration, the surfactant adsorption occurred mainly due to ion exchange. When the surfactant concentration exceeds 0.8%, the adsorption increment rate becomes lower with the increase of surfactant concentration. This shows that the adsorption has to overcome the electrostatic repulsive force between surfactant and the similarly charged solid in these surfactant concentrations. We also can see the from the plot, at point surfactant concentration is 1%, the saturation of surfactant adsorption is almost reached. The saturation adsorption was estimated at 3 mg/g sand. It can be concluded that the surfactant adsorption increases as the surfactant increases until it reaches saturation adsorption. The optimum concentration of surfactant that is chosen is 0.6% due to the further increment in surfactant concentration will not give big different in surfactant adsorption.

2<sup>nd</sup> phase: To find optimum concentration of alkali

Table 2 : To find optimum concentration of alkali

Alkali Concentration (%)	0	0.2	0.4	0.6	0.8	1
Surfactant concentration (%)	0.6	0.6	0.6	0.6	0.6	0.6
Weight of surfactant(g)	0.12	0.12	0.12	0.12	0.12	0.12
Volume of Brine(ml)	20	20	20	20	20	20
Density(g/cc)	1.068	1.0688	1.0693	1.0701	1.0713	1.072
pH	7.4	9.88	10.1	10.3	10.6	11
Weight of sand(g)	21.36	21.376	21.386	21.402	21.426	21.44
Molarity of surfactant solution(M)	0.016807	0.016807	0.016807	0.016807	0.016807	0.016807
Volume of surfatant solution(3 day	4	4	4	4	4	4
Used Hyamine (ml)	10	11	11.5	12.5	12.5	13
Molarity of surfactant solution(M)	0.01	0.011111	0.011765	0.0125	0.012698	0.012903
Convert to %	0.357	0.396667	0.42	0.44625	0.453333	0.460645
Surfactant Remaining (mg)	71.4	79.33333	84	89.25	90.66667	92.12903
Surfactant Lost (mg)	48.6	40.66667	46	30.75	29.33333	27.87097
Surfactant Lost /Weight of Sand (m	2.275281	1.902445	1.683344	1.436782	1.369053	1.299952

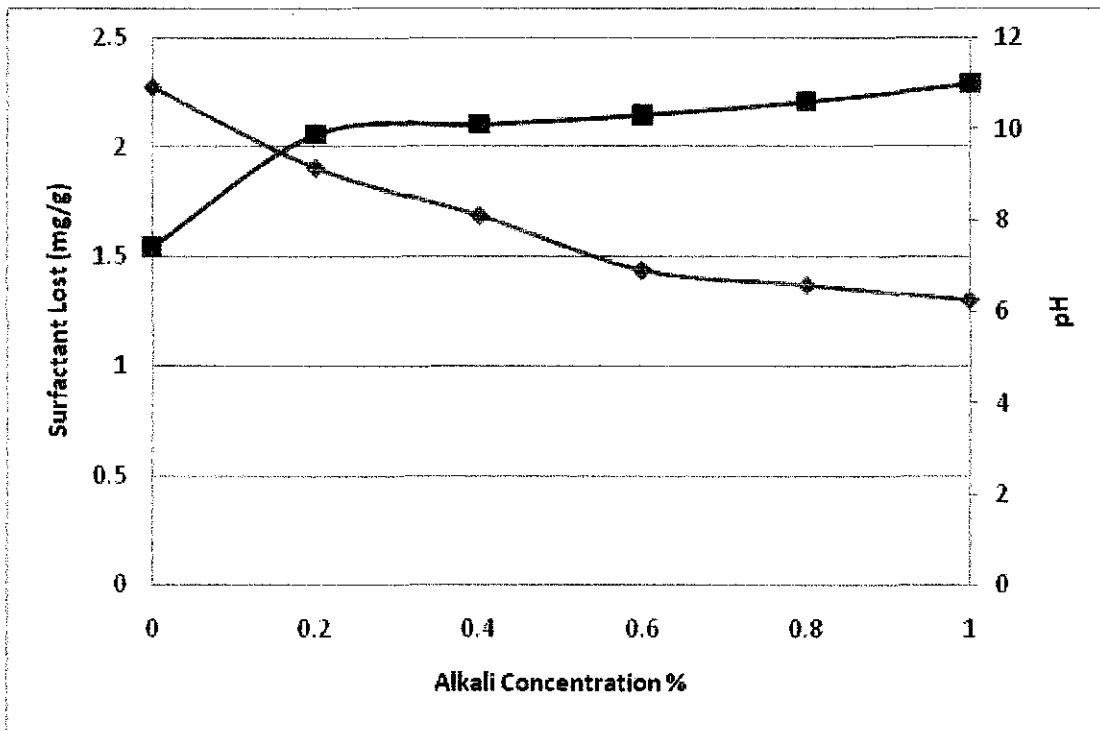


Figure 2: To find optimum concentration of alkali

Figure 2 shows the effect of alkali on surfactant adsorption with the use of brine water. As we can see from the table 2, different concentration of sodium carbonates had been used which are 0.2, 0.4, 0.6, 0.8, and 1% with 0.6% of surfactant concentration. From the plot, the blue line is for surfactant lost versus alkali concentration and the red line is for pH versus alkali concentration. From the plot, we can see that the surfactant adsorption decreases as alkali concentration increases. This is due to the high pH will make the sand surface becomes more negative, though will create repulsion force to avoid surfactant be absorbed by the sand. As we can from the plot, at 0 % of alkali, the surfactant adsorption is at 2.3 and when the alkali is introduced into the system, the surfactant adsorption is at 1.7. This is due to the increment in pH value from 7.4 to 10. From the plot, we can see the saturation adsorption at 0.6% of alkali concentration which is the optimal concentration. Further increment in alkali concentration over 0.6% is not drastically reducing the surfactant adsorption. For optimal concentration of alkali, I chose 0.6%.



3<sup>rd</sup> phase: To find optimum concentration of acid

Table 3: To find optimum concentration of acid

Acid Concentration	0	0.2	0.4	0.6	0.8	1
Alkali Concentration (%)	0.6	0.6	0.6	0.6	0.6	0.6
Surfactant concentration (%)	0.6	0.6	0.6	0.6	0.6	0.6
Weight of surfactant(g)	0.12	0.12	0.12	0.12	0.12	0.12
Volume of Brine(ml)	20	20	20	20	20	20
Density(g/cc)	1.0703	1.0711	1.0723	1.0729	1.0736	1.0738
pH	10.15	9.33	8.55	7.64	6.52	6.02
Weight of sand(g)	21.406	21.422	21.440	21.458	21.472	21.476
Molarity of surfactant solution(M)	0.0168	0.01681	0.01683	0.0168	0.0168	0.0168
Volume of surfatant solution(3 days) taking for test	4	4	4	4	4	4
Used Hyamine (ml)	12.5	12	11.5	11	10	9
Molarity of surfactant solution(M)	0.0125	0.01194	0.01136	0.011	0.01	0.009
Convert to %	0.4463	0.42627	0.4139	0.3927	0.357	0.3213
Surfactant Remaining (mg)	89.25	85.2537	82.78	78.54	71.4	64.26
Surfactant Lost (mg)	30.75	34.7463	37.22	41.46	48.6	55.74
Surfactant Lost /Weight of Sand (mg/g)	1.4365	1.62199	1.7354	1.9321	2.2634	2.5955

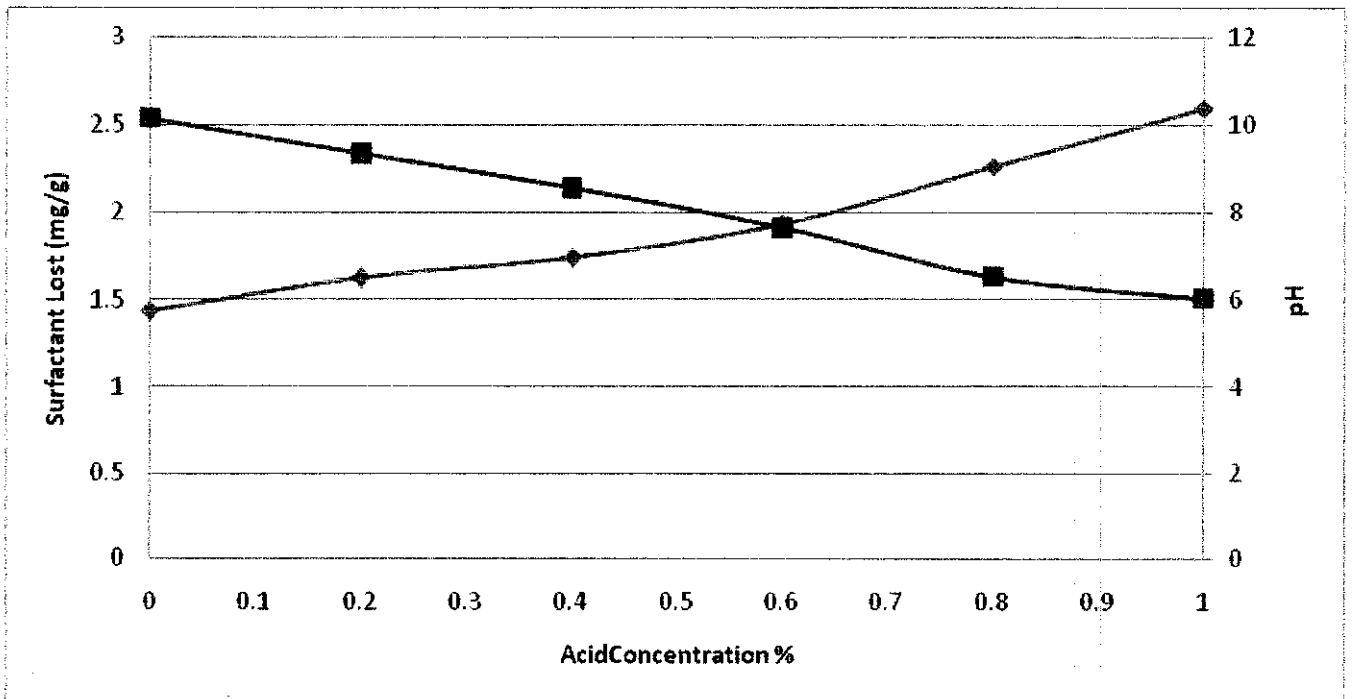
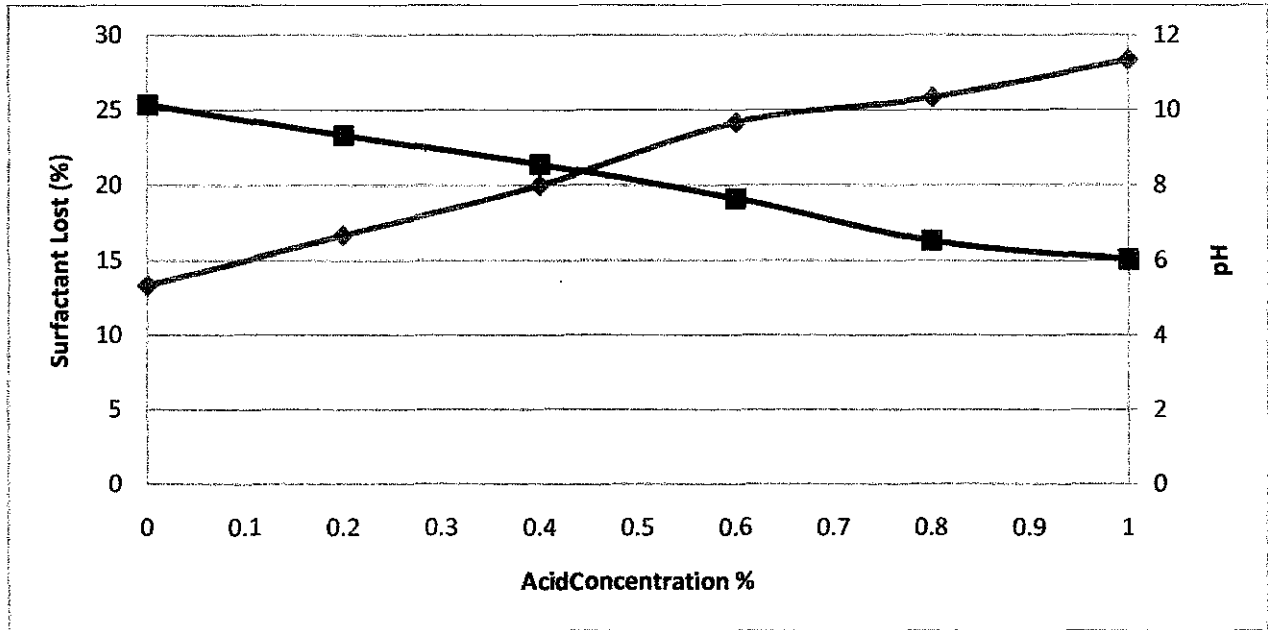


Figure 3: To find optimum concentration of acid

From the plot, the blue line is for surfactant lost versus alkali concentration and the red line is for pH versus alkali concentration. It shows the effect of acid on surfactant adsorption with the

use of brine water. Different concentration of acid acrylic had been used which are 0.2, 0.4, 0.6, 0.8, and 1% with 0.6% of surfactant and 0.6% alkali concentration. From the plot, we can see that the surfactant adsorption increases as acid concentration increases. This is due to the lower pH will make the sand surface becomes less negative, though will create low repulsion force to avoid surfactant be absorbed by the sand. As we see the plot, at 0 % of acid, the surfactant adsorption is at 1.43 and when the acid is introduced into the system, the surfactant adsorption is at 1.6. Ph changes from 10.15 to 9.3. But, we can conclude the surfactant adsorption is lesser compared to the surfactant without alkali and acid

## Dynamic Method Result:



From the plot, the blue line is for surfactant lost versus alkali concentration and the red line is for pH versus alkali concentration. It shows the effect of acid on surfactant adsorption with the use of brine water. Different concentration of acid acrylic had been used which are 0.2, 0.4, 0.6, 0.8, and 1% with 0.6% of surfactant and 0.6% alkali concentration. From the plot, we can see that the surfactant adsorption increases as acid concentration increases. This is due to the lower pH will make the sand surface becomes less negative, though will create low repulsion force to avoid surfactant be absorbed by the sand. As we see the plot, at 0 % of acid, the surfactant lost is 13% from original weight and when the acid is introduced into the system, the surfactant lost is at 18%. Ph changes from 10.15 to 9.3. But, we can conclude the surfactant adsorption is lesser compared to the surfactant without alkali and acid. The surfactant adsorption is lesser compared to static method due to the time constraint during flow test. We did not give enough time for surfactant adsorption process since surfactant adsorption process also depends on flow rate.

## **9. Conclusion**

Surfactant adsorption increases as surfactant concentration increases until it reaches saturation adsorption. This is proven in 1st part of the experiment. We also can conclude that the surfactant adsorption is depending on pH of the surfactant solution. Increment of pH of the solution will reduce surfactant adsorption which is the function of alkali to reduce pH of solution which is proven in 2nd part of the experiment. We can see the precipitation inhibitor will increase the surfactant adsorption by reducing the pH of the solution. However, with further increases of acid concentration, the surfactant adsorption increases gradually but it is still lower compared to without appearances of acid and alkali.

## 10. Appendix

### Appendix A

Surfactant solution;

1. The weight needed for AOS is calculated like below;

For example; To make 0.2% of surfactant solution in 100 ml of brine

$$\text{Concentration} = \text{Mass/volume} * 100$$

$$m = (0.2/100) * 100$$

$$m = 0.2 \text{ g}$$

So to make 0.2 % of surfactant solution in 100 ml of brine, we need 0.2 g of surfactant

*\*This calculation is applicable for acid and alkali*

2. Alpha olefin sulfonate is weighted by using mass balance.
3. Pour the volume needed for brine in a beaker and mix weighted AOS into the brine.
4. Stir the solution with magnetic stirrer for 5 minutes.
5. For different components like acid and alkali, the priority of mixing is acid, alkali and surfactant.

## Appendix B

The brine is prepared based on the  $\text{Na}^+$ ,  $\text{Mg}^{2+}$  and  $\text{Ca}^{2+}$  ions. Since the salt is in formed of chloride and chloride hydrate, molecular weight fraction is needed to calculate the amount of salt needed to prepare such brine. In this example, calculation for brine with hardness salinity of 5000 ppm will be shown:

Molecular Weight for  $\text{NaCl}$  = 58.44 g/mol

Molecular Weight for  $\text{MgCl}_2 \cdot \text{H}_2\text{O}$  = 203.31 g/mol

Molecular Weight for  $\text{CaCl}_2 \cdot \text{H}_2\text{O}$  = 147.02 g/mol

Molecular Weight for  $\text{Na}$  = 22.98977 g/mol

Molecular Weight for  $\text{Mg}$  = 24.3050 g/mol

Molecular Weight for  $\text{Ca}$  = 40.078 g/mol

Amount of ions weight needed for 5000 ppm brine:

5000 ppm = 5 g (ions) / 1 L (distilled water)

Hardness of  $\text{Mg}^{2+}$  and  $\text{Ca}^{2+}$  are chosen at 500 and 400 ppm respectively.

500 ppm ( $\text{Mg}^{2+}$ ) + 400 ppm ( $\text{Ca}^{2+}$ ) + 4100 ppm ( $\text{Na}^+$ ) = 5000 ppm

Also equivalent to

$[0.5\text{g} (\text{Mg}^{2+}) + 0.4\text{g} (\text{Ca}^{2+}) + 4.1\text{g} (\text{Na}^+)] / 1 \text{ L} = 5\text{g} (\text{ions}) / 1 \text{ L} = 5000 \text{ ppm}$

To calculate NaCl needed for above mass:

$$\text{Mass Na} = (\text{MW Na} / \text{MW NaCl}) * \text{mass NaCl}$$

$$\text{Mass NaCl required} = \text{Mass Na} * 1/(\text{MW Na} / \text{MW NaCl})$$

$$= 4.1\text{g} * 1 / (22.98977/58.44)$$

$$= 10.422 \text{ g}$$

To Calculate MgCl<sub>2</sub>.H<sub>2</sub>O needed fo above mass:

$$\text{Mass Mg} = (\text{MW Mg} / \text{MW MgCl}_2\cdot\text{H}_2\text{O}) * \text{mass MgCl}_2\cdot\text{H}_2\text{O}$$

$$\text{Mass MgCl}_2\cdot\text{H}_2\text{O required} = \text{Mass Mg} * 1/(\text{MW Mg} / \text{MW MgCl}_2\cdot\text{H}_2\text{O})$$

$$= 0.5\text{g} * 1/ (24.3050/203.31)$$

$$= 4.18 \text{ g}$$

To Calculate CaCl<sub>2</sub>.H<sub>2</sub>O needed fo above mass:

$$\text{Mass Ca} = (\text{MW Ca} / \text{MW CaCl}_2\cdot\text{H}_2\text{O}) * \text{mass CaCl}_2\cdot\text{H}_2\text{O}$$

$$\text{Mass CaCl}_2\cdot\text{H}_2\text{O required} = \text{Mass Ca} * 1/(\text{MW Ca} / \text{MW CaCl}_2\cdot\text{H}_2\text{O})$$

$$= 0.4 \text{ g} * 1/ (40.078/147.02)$$

$$= 1.467 \text{ g}$$

## Appendix C

For example;

Surfactant Concentration before the test = 0.6 %

Mass of surfactant= 0.12 g

Volume of brine= 20 ml

AOS molecular weight= 357 g/mol

Mass of sand= 21.06 g

### From the two phase titration method

Used Hyamine= 13.5- 10= 3.5 ml

Surfactant volume used for the test= 4 ml

To calculate the molarity of surfactant;

$$M_1 V_1 = M_2 V_2$$

Where;

$M_1$  = Molarity of titrant

$V_1$  = Volume of titrant

$M_2$  = Molarity of titrated solution

$V_2$  = Volume of titrated solution

So, substitute the value into the calculation;

$$M_2 = \frac{0.004 \times 3.5}{4}$$

$$M_2 = 0.0035$$



Then, to convert molarity to % concentration

$$\begin{aligned}\% \text{ concentration} &= (0.0035 * 357/1000) * 100 \\ &= 0.1249 \%\end{aligned}$$

To find the surfactant in mg

$$\text{Mass} = (0.1249/100 * 20) * 1000$$

$$\text{Mass} = 24.98 \text{mg}$$

Surfactant Lost in mg

$$\text{Mass lost} = (0.12 * 1000) - 24.98$$

$$\text{Mass lost} = 95.02 \text{ mg}$$

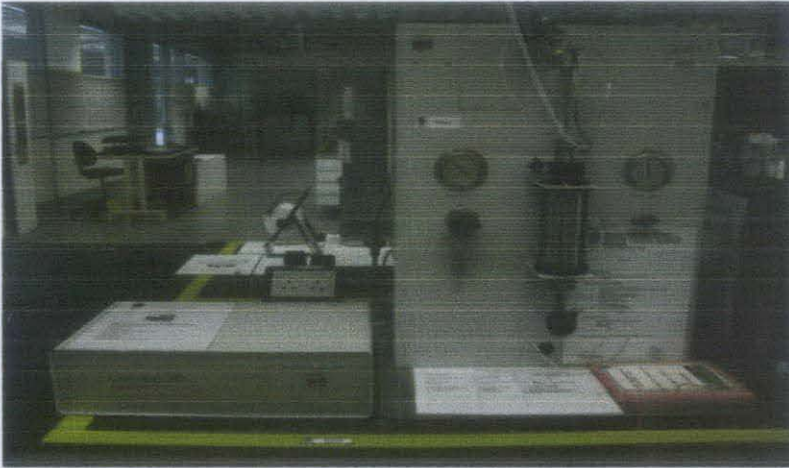
Surfactant Lost over mass of sand

$$= 95.02/21.406$$

$$= 4.43 \text{ mg/g sand}$$

## Appendix D

Equipment Used;



Poroperm



Benchtop Permeability System



Mass Balance



Oven



Magnetic Stirrer



Density Meter

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